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Guidance for the Analysis of Refinery Wastes

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of

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1.0 BACKGROUND

1.1 Listing

Section 261.11 sets out the criteria used by EPA to whether wastes should be listed as hazardous. All wastes listed as hazardous meet at least one of these criteria which encompasses the terms of Section 1004(5) of RCRA. The criterion used most often is 261.11(a)(3), which indicates that any waste containing any of the toxic constituents listed in Appendix VIII of Part 261 shall be listed unless, upon consideration of certain enumerated factors, the waste is not capable of posing a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported or disposed, or otherwise managed. The regulation also provides that Administrator may list classes or types of wastes if there is a reason to believe that wastes within the class or type are typically or frequently hazardous.

1.2 Delisting

§260.20 of the regulations allows any person to petition the Administrator to modify or revoke any provision of Parts 260 through 265, 124, 270, and 271 of Title 40 of the Code of Federal Regulations. In addition, §260.22 specifically provides generators the opportunity to petition the Administrator to exclude listed wastes on a "site-specific basis."

1.3 Land Treatment

40CFR Part 264.272 requires that owners/operators of a hazardous waste land treatment unit demonstrate that their waste is degraded, transformed, or immobilized in the treatment zone. Prior to receiving a permit to operate such a facility. §264.271 requires that the facility permit list the wastes that can be managed by the facility and the hazardous constituents that must be degraded, transformed, or immobilized. Hazardous constituents are those constituents listed in Appendix VIII of Part 261, which are reasonably expected to be in, or derived from waste placed in or on the treatment zone of the land treatment unit.

1.4 Permits

The submission requirements for a Part B RCRA Permit application as given in §270.14 include the requirement for information on chemical and physical analysis of the hazardous waste to be handled at the facility. In order to ensure successful treatment, storage, or disposal of the waste, a waste analysis plan must be submitted as specified under §270.14(b)(3) and §264.13. The waste analysis plan must include procedures for screening wastes for consistency with manifests, to monitor for the presence of restricted wastes, and to analyze for reactive, ignitable, or incompatible wastes. The specific waste analysis requirements given in Part 264 for different types of facilities have other objectives, including: determining compatibility of

the waste with facility liners and other equipment; documenting removal or decontamination at closure and identifying residuals left in place; and, identifying Part 261, Appendix VIII constituents in waste as part of a land treatment demonstration.

1.5 Purpose of the Document

The EPA is conducting an industry study under the auspices of Section 3007 of the RCRA to determine if the various classes and types of wastes from the petroleum refining industry are typically or frequently hazardous.

This study has produced two observations covering waste characterization:

° Analysts will tend to follow a regulatory procedure as closely as possible. Though, this process has a benefit when attempting to compare results across different strata such as samples, analysts, and laboratories, it may be a liability when the sample is such that certain aspects of the analytical procedure present conditions not anticipated by the method.

° Samples derived from waste streams challenge the method in ways which necessitate common sense modifications to the analytical approach.

This guidance document is meant as a companion to SW-846. It describes and directs the modifications applied to samples from petroleum refining waste streams. The experience gained by EPA and the Refinery Industry should be applied to determining analytes in refinery effluent for listing, delisting, permitting, and land treatment.

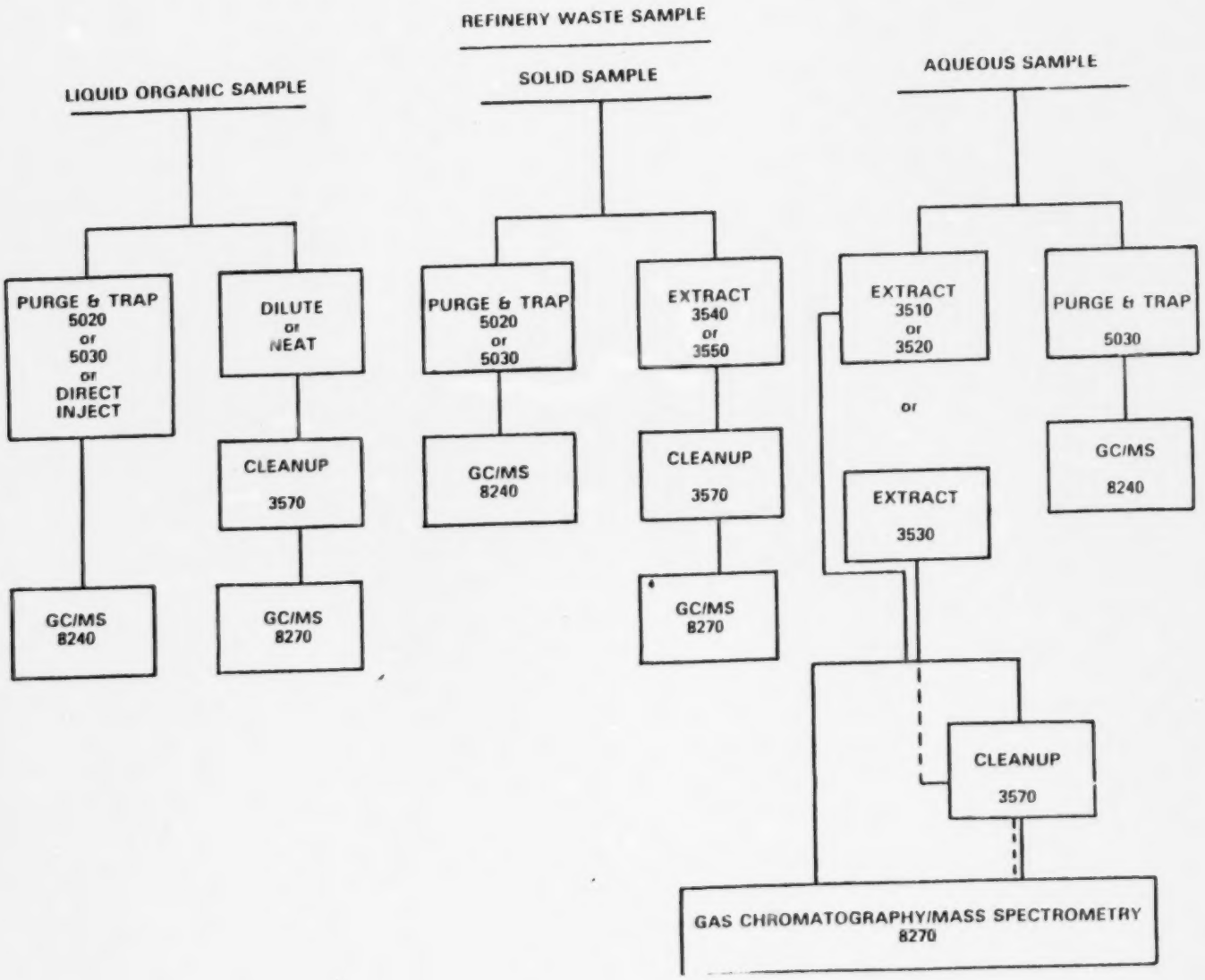
1.6 Use of the Guidance Document

This guidance document describes the analytical constraints imposed by waste stream residual samples as contrasted to what can be described as environmental residual samples. It indicates which SW-846 procedures to use and the options which should mitigate these analytical constraints.

Figures 1 and 2 are flow-charts for the analytical methods from SW-846 employed in these studies. The flow charts include all methods which would be required and recommended for the analysis of refinery samples. Some methods may be omitted because they are not required due to the matrix or phase of a given sample. Other methods from SW-846 may be included if the analytical conditions dictate that such methods would be more effective in a particular analytical situation.

Section 2 discusses the sampling, preservation, and handling of refinery samples. It discusses method selection as a function of waste, analyte and analyte concentration.

Figure 1: Schematic representation of the determination of organic constituents in petroleum refinery samples



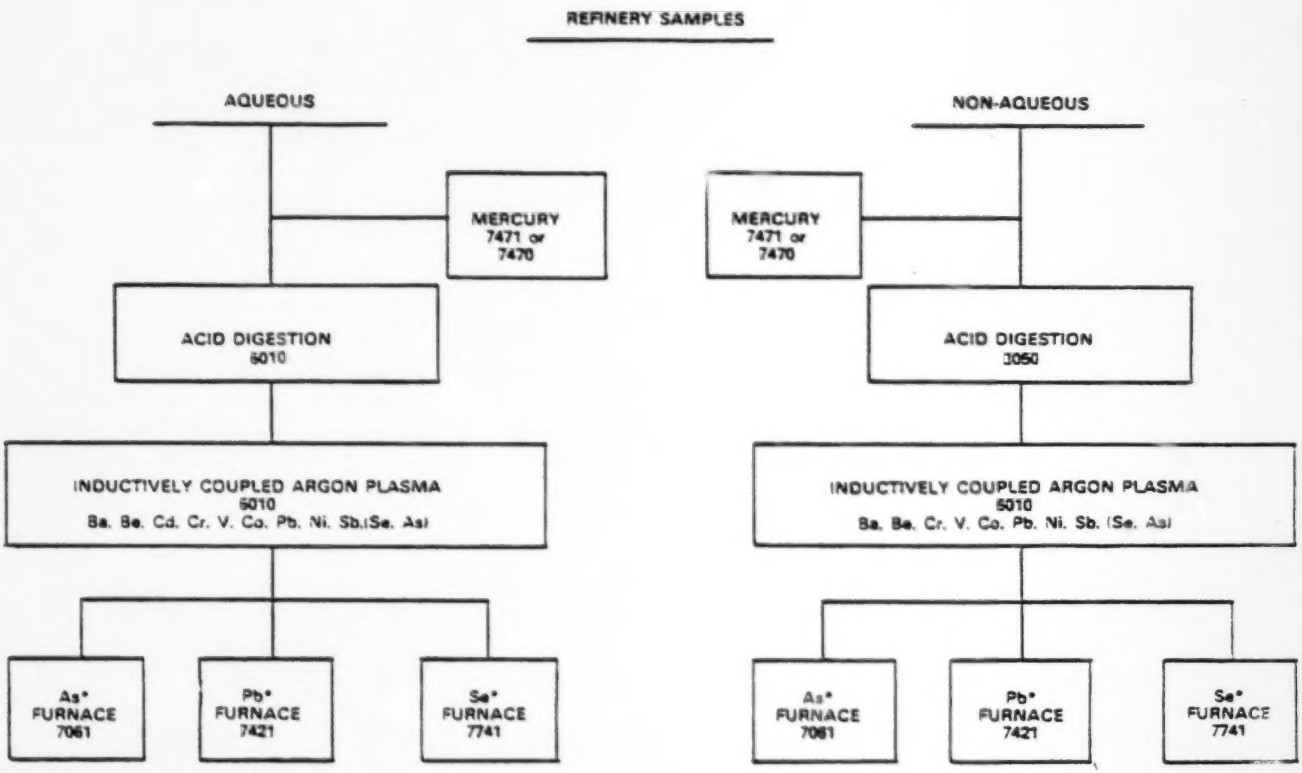


Figure 2: Schematic representation of the determination of metals in refinery samples.

Section 3 discusses extraction procedures for samples and clean-up procedures for extracts. Extraction procedures use those techniques which separate the analytes from the gross matrix. They include digestions, extractions, dilutions and chelations. Sample work-up includes separation of analytes from interferences i.e., chromatographic clean-up of samples subsequent to separation from the matrix.

Section 4 describes the manipulations required of the SW-846 determinative procedures for organic analytes and metal analytes because of refinery waste characteristics.

Section 5 discusses the application of indicator analyses in the characterization of refinery residuals. These include the determination of percent water, oil and solids and the determination of total organic carbon in refining residuals.

Section 6 presents the quality control requirements for the determination of Appendix VIII constituents in refinery residuals. Quality control procedures are included with the expectation that they will provide a means of determining and improving the information content of the data presented. Quality control procedures are intended to be an integral part of the analytical scheme. Successful completion of any analysis depends on the evaluation of quality control information. The extent to which this information is required is inversely proportional to the consistency of and knowledge about the matrix and the

predictability of the interaction of the analyst, the sample and the method.

Section 7 enumerates the deliverables required as a result of an analysis. The intent of specifying the deliverables is to assure that all components of the data are available for validation of the data, evaluation of the quality and interpretation of the results.

2.0 SAMPLE CHARACTERIZATION

2.1 Sample Receipt and Handling

SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, presents general sample collection and shipping requirements for solid waste samples. SW-846 should be consulted concerning these protocols. Table 1 summarizes sample sizes and on-site preservation techniques to be used for refinery samples. The amount of sample required* and the preservation technique selected are dependent upon the analyses to be performed. The table assumes all analyses are performed on each waste. For samples which require only one or two tests, relatively less sample may be needed. Samples may collected in duplicate. The duplicate sample provides additional material should additional analyses be required. They may be used

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* While a detection limit of 1 ppm may be required, if the level in the waste stream is anticipated to be 10,000 ppm (1%), it is not useful to select a sample for analysis based on the requirement of a 1 ppm detection limit for that analyte.

to perform the required QA/QC, serve as backup in the event of breakage or for determining selected residuals when low levels of analytes must be determined.

2.2 Preservation

Preservation techniques are applicable to both field and laboratory conditions. The requirements for refinery residuals presented for on-site preservation are identical to those required for storage in the laboratory. These preservation requirements are outlined in SW-846 and are summarized in Table I.

2.3 Representativeness

All analytical data are reported based on the wet weight of sample, unless otherwise specified. Multiphase samples must be homogenized before the sample is aliquoted so that the aliquot taken is representative of the total sample. SW-846 presents sampling techniques and methods for obtaining a representative sample. The basic principles presented may be used by analysts as a guide for subsampling. For samples containing water (other than aqueous samples) the percent water must be determined on a representative subsample so that constituent concentrations can be determined on a dry weight basis if required.

2.4 Holding Times

The analytes to be determined dictate the maximum holding time for each sample. Table 1 summarizes the sample types for refinery samples, maximum holding times

(time of collection) and associated field preservation techniques. The holding times required for refinery samples are based on protocols published in SW-846. Many of the petroleum refinery wastes are multiphasic wastes containing water. These samples may be susceptible to biodegradation which necessitates relatively brief holding times. The holding times presented here are based on representative samples and are designed to meet the needs of the majority of analyses.

3.0 EXTRACTION AND CLEAN-UP PROCEDURES

3.1 Introduction

The primary analytical thrust of SW-846 is towards the residual or trace sample, i.e., samples are extracted or digested, separated and determined as though the matrix was chemically dis-similar to the analyte and that the bulk of potential interferants can be discriminated from the analyte by judicious selection of chromatographic conditions or determinative procedures. While such conditions may exist in waste streams, the opposite of these conditions also exist, as the Refinery Study indicates. That is, the matrix may be chemically similar to the analyte. Potential interferants and analytes may be present in amounts which would overwhelm procedures employing residue techinques. The modification to the SW-846 methods which are required are the analytical common sense approaches to these problems. Waste stream

TABLE 1. REFINERY SAMPLE TYPES, COLLECTION, AND PRESERVATION PROTOCOLS

SAMPLE TYPE	COLLECTION METHOD	TYPE OF ANALYSES	MINIMUM REQUIRED SIZE	SAMPLE CONTAINERS (per sample set)	PRESERVATION[1]	MAXIMUM HOLDING TIME
Bioactive Solids	Tap, Trier, Dipper, or Auger	Conventional EP Extraction	≤ 100 g	A	4°C	
		GC/MS for Semivolatiles	100 g	A	4°C	14/40[3]
		Total Metals	≤ 100 g	B	4°C	180[2]
		GC/MS for Purgeables	40 mL	C	4°C	14
Oily Emulsions and Tars	Tap, Trier, Coliwasa Weighted Bottle, or Dipper	Oily Waste EP Extraction	≥ 100 g	A	4°C	180[2]
		Total Metals	0.5-1.0 g	B		180[2]
		GC/MS for Semivolatiles	100 g	A	4°C	14/40[3]
		Oil, Water, Solids	150 g	A	4°C	45
		GC/MS for Purgeables	40 mL	C	4°C	14
Spent	Thief, Scoop and Shovel, Trier or Auger	Oily Waste or Conventional EP Extraction	≤ 100 g	A	4°C	
		GC/MS for Semivolatiles	100 g	A	4°C	14/40[3]
		GC/MS for Purgeables	40 mL	C	4°C	

1/ 4°C denotes refrigeration or storage on ice.

2/ Hg holding time: 38 days in glass container; 13 days in plastic container

3/ Sample/Extract Holding Time

A = Two 1 L wide mouthed jars - (Teflon lid)
B = Two 0.5 bottles
C = Two 40 mL VOA bottles

TABLE 1. REFINERY SAMPLE TYPES, COLLECTION, AND PRESERVATION PROTOCOLS

SAMPLE TYPE	COLLECTION METHOD	TYPE OF ANALYSES	MINIMUM REQUIRED SIZE	SAMPLE CONTAINERS (per sample set)	PRESERVATION[1]	MAXIMUM HOLDING TIME
Aqueous Liquids	Tap, Dipper, Coliwasa, or Weighted Bottle	Total Metals	500 mL	B	pH < 2 HNO_3	180
		GC/MS for Purgeables	40 mL	C	4°C	14
		GC/MS for Semivolatiles	1 L	A	4°C	14
Oily Liquids	Tap, Dipper, Coliwasa, or Weighted Bottle	Total metals	0.5-1.0g	B		180
		GC/MS for semivolatiles	≤ 100 g	A	4°C	14
		Oil, Water, Solids	150 g	A	4°C	45
		GC/MS for Purgeables	40 mL	C	4°C	
Oily Sludges	Scoop and Shovel, or Trier	Oily Waste EP Extraction	≤ 100 g	A	4°C	
		Total Metals	0.5-1.0 g	B		180
		GC/MS for Semivolatiles	≤ 100 g	A	4°C	14/40[3]
		Oil, Water, Solids	150 g	A	4°C	45
		GC/MS for Purgeables	40 mL	C	4°C	
Dry Solids	Thief, Scoop and Shovel, Trier, or Auger	Oily Waste or Conventional EP Extraction	≥ 100 g	A	4°C	
		Total Metals	0.5-1.0 g	B		180
		GC/MS for Semivolatiles	< 100 g	A	4°C	

TABLE 2. SUMMARY OF ANALYTICAL - PROTOCOL FOR REFINERY RESIDUALS

ANALYTICAL CATEGORY	DETERMINATIVE METHOD	CLEAN-UP METHOD	EXTRACTION METHOD	SAMPLE TYPE
Metal	6010	--	3020	Aqueous liquid
	7471	—	7471	Aqueous extract
	7061, 7421, 7741*	—	3050	Oily liquids Dry solids Oily sludge Bioactive solids Oily emulsions Tars Spent catalysts
Volatiles	8240	—	5030	All sample types
Semivolatiles**	8270	3530/3570	3510/3520	Aqueous
		3570	dilution	Oily liquids
		3570	—	
		3570/3530	3550/3540 or dilution	Oily sludge
		3570/3530	3550/3540	Solids (dry, bioactive, other)
		3570/3530	3550/3540 or dilution	Oily emulsions and tars
EP Toxics	See aqueous extracts and oily liquids as appropriate		1310	All except aqueous
Oily Waste EP (Delisting Only)			1330	All except aqueous

* If required.

** SW-846 should be consulted for additional determinative methods intended for subsets of compounds, i.e., 8330, 8060, for PAH's.

conditions require modification of what are essentially residue methods to a more component oriented determination while maintaining the sound technical bases of the analyses.

3.2 Metals

Most refining samples are prepared for total metal determination by Method 3050 (HNO_3/H_2O_2 digestion procedure). Most refinery samples are difficult to dry for use in Method 3050 and an amount of wet sample equivalent to 1 gram on a dry weight is used.

The THF/Toluene extract from the Oily Waste EP (Method 1330) is evaporated to near dryness prior to digestion by Method 3050.

The aqueous samples and aqueous EP extracts are digested using the Method 6010 digestion procedure.

3.3 Organic Analytes

The choice of an extraction method is dictated by the chemical and physical state of the sample. Aqueous liquid samples would be amenable to the liquid-liquid extraction procedures. Selection between Methods 3510, 3520, and 3530, 3540 and 3550 would be a function of the anticipated interferences and the analyte to be determined. The choice may also depend on the availability of automated equipment or the tendency of one method to form an intractable emulsion compared to the other method or the need to separate acid components from basic components.

Many refinery samples contain significant amounts of

extractable compounds necessitating a large solvent to sample ratio. For these methods and the foregoing analytical conditions, a 1 gram sample was used. In Method 3530, the acid base extraction, the sample is initially extracted with 100 ml of solvent followed by two 30 ml portions. A 300 ml volume of solvent is used in Method 3540, the Soxhlet extraction. A 1 gram, sodium sulfate dried sample is extracted with 100 ml of solvent in Method 3550, the sonication extraction.

3.3.1 Organic Clean-Up

Many of the extracts of complex samples need to be cleaned-up to reduce analytical interferences and provide reasonable detection limits. SW-846 outlines clean-up procedures to be used for petroleum refining residuals. These methods are designated as preparatory techniques for both organic and inorganic analyses. In some cases, several clean-up steps may be necessary to adequately prepare the sample extracts for analysis. Section I presents an overview of the analysis flows schemes to be used for both organic and inorganic analyses. It should be consulted in the selection of clean-up methods.

Method 3570, Column Clean-up for Oily Wastes, is used following any of the five extraction procedures (Methods 3510 to 3550). Most refinery residuals contain high concentrations of aliphatic hydrocarbons. These constituents, for the most part, are not of interest in assessing whether or not a waste is hazardous. The column clean-up

method is designed to reduce the interference of aliphatic hydrocarbons and permit detection of the compounds of interest with relatively good precision.

4.0 DETERMINATIVE METHODS

4.1 Metals

Inductively Coupled Plasma (ICP) emission spectroscopy, Method 6010, may be used as the primary quantitative method (Table 2 and Figure II) for characterizing the metals content of petroleum refinery residuals. The appropriate atomic absorption method may be substituted because of equipment availability or interferences with the ICP method due to high concentrations of metals. The cold vapor furnace AA, Method 7471, is to be used in mercury determinations because of possible mercury loss in Method 6010. Arsenic is determinable by Furnace AA Method 7061. Selenium is determinable by Furnace AA, Method 7741. Lead is determinable by Furnace AA, Method 7421. These should be used when ICP indicates "not detected" but the detection limit is above the required limit.

4.2 Organic Analytes

The organic analytical methods to be used in this program are presented in SW-846. Two GC/MS analyses are used to identify and quantify purgeable compounds and semivolatile compounds. For selected samples, HPLC may be performed to determine the concentration of various PNA's.

4.2.1 Method 8240

This Method will be used for the analysis of purgeable constituents. The following modifications are made to the method in SW-846.

. In Section 5.2 and all following sections tetraglyme (tetraethylene glycol dimethyl ether) should be substituted for PEG. Tetraglyme can be purified in the manner presented in the method for PEG.
. The surrogate standards and internal standards (minimum required) to be used are listed in Table 3.
. The GC/MS spectra will be searched for the compounds listed as analytes pertinent to refinery wastes and identified as VOA's as well as the 10 Appendix VIII compounds which are detected in the highest concentration.

4.2.2 Method 8270

Method 8270 will be used for the analysis of semi-volatile organic constituents. The following modifications are to be made to the method.

. The surrogate standards and internal standards to be used are listed in Table 4.
. The GC/MS spectra will be searched for the compounds listed as analytes pertinent to refinery wastes and identified as semi-volatile organic compounds as well as the 10 Appendix VIII compounds which are detected in the highest concentration.

5.0 Bulk Properties Determinations

The Percent Oil, Water and Solids Methods and the Total Organic Carbon are used to measure bulk properties of petroleum refining residuals. These tests are performed to optimize other tests or to provide information in the early stages of the analysis.

5.1 The Percent Water and Percent Solids Methods

The following references may be used in selecting an appropriate bulk properties test method:

5.1.1. Percent Oil

- Standard method for the Examination of Water and Wastes, 14th edition, p. 515, Method 502A, (1975).
- Standard Methods for the Examination of Water and Wastes, 14th edition, p. 516, Method 502B, (1975).
- American Petroleum Institute, "Manual on Disposal of Refining Wastes," vol. IV, Method 733-758, (1958).

5.1.2. Percent Water

- ASTM D-95
- Analytical Chemistry, 31, 215 (1959)

5.1.3. Percent Solids

- Solid residue of the Oily Waste EP

TABLE 3

Characteristic Ions for Surrogate and Internal Standards for Volatile Organic Compounds

Compound	Primary Ion M/z	Secondary Ion(s) M/z
Surrogate Standards		
4-Bromofluorobenzene	95	174,176
1,2-Dichloroethane-d_4	65	102
Toluene d-8	98	70,100
Internal Standards		
Bromochloromethane	128	49,130,51
1,4-difluorobenzene	114	63,88
Chlorobenzene-d_5	117	82,119

5.1.4. Total Organic Carbon

. Method 9060, SW-846 2nd Edition.

It is expected that the requirement for TOC will be in environmental samples or aqueous samples.

6.0 QUALITY CONTROL

The basic level at which analytical quality control operates is the analytical batch. The analytical batch is comprised of samples of the same matrix which are analyzed for the same constituents together or in sequence by the same personnel using the same methods.

6.1 Using Quality Control Data

The data acquired by instituting quality control procedures can be used to estimate the information content of the analytical data.

Surrogates data provide a consistent and on-going assessment of the matrix-method-laboratory interaction. Surrogates do not necessarily reflect how well individual analytes are determined but are an indicator of how well the analytical process has been carried out. Average surrogate recoveries for the analytical batch, standard deviations of the average recovery provide an instantaneous evalution of analytical quality in terms of accuracy and precision. This can be extrapolated to specific analytes only by assumption or if the analytical behavior of the analyte has been correlated to the analytical behavior of the surrogate.

When these averages and standard deviations are tracked as a function of time within laboratories or across laboratories, estimates of batch to batch precision and interlaboratory precision can be estimated. This can be done through calculation of pooled standard deviations or through construction of control charts for the tracked analyte or variable.

The use of actual compounds spiked into samples and duplicates of spiked samples allows the data user to determine the analytical behavior or actual analytes in terms of accuracy, replicability and repeatability and the sample-to-sample precision of specific analytes.

6.2 Quality Control Program for the Analysis of RCRA Samples

The objective of an analytical quality control program is to develop information. This information can be used in the following ways.

- Evaluate the information content of analytical data

  The determination of accuracy and precision of analytical data are necessary in order to make legal, health or engineering decisions which are based in part or wholly on analytical data.

- Provide a means for judging when to evaluate alternative corrective actions

  Quality maintenance is an integral part of laboratory management as it is with the management of any manufacturing process. In order to maintain the quality of the analysis process one must define it in terms of

TABLE 4

Characteristic Ions for Surrogates and Internal Standards for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion(s)
	M/z	M/z
Surrogate Standards		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4-6-Tribromophenol	330	332, 141
Nitrobenzene-d_5	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
Internal Standards		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenapthene-d_8	164	162,160
Phenanthrene-d_8	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

controlling variables or variables which are indicative of quality level of the process.

° Determining the effect of corrective actions

Using the quality control information generated, it is possible to identify and correct systematic errors. One gauges the effect of corrective actions on controlling variables or other measures of quality.

Quality control is another management tool used to generate and evaluate information. What is unique about quality control is that it requires the creation and operation of processes which are parallel to the production of the end product--the analytical result. The justification of any of the allied quality control procedures must be in terms of their ability to maximize the information content of an analytical result in terms of the use of the result, i.e., the information content or the degree of quality must be appropriate to the use.

6.3 Components of Quality Control

It is essential to incorporate quality control procedures into sample analysis. Quality control procedures in an analytical study or project are to provide a means of measuring the information content of the data generated by the analysis.

6.3.1 Analytical Quality Control

The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together using the same

method sequence, the same lots of reagents and having the manipulations common to each sample executed by the same personnel within the same time period or in continuous sequential time periods. Samples, themselves, should be of similar composition. The following components of analytical quality control are related to the analytical batch.

Blank: An artificial sample designed to monitor the the introduction of artifacts into the analytical process.

Spiked blank: A blank which has been spiked with the analyte(s) to monitor the execution of the analytical method. The level of the spike should be at the regulatory action level.

Field Sample: Representation of a large body of material.

Spiked sample: Sample spiked with analyte(s) to monitor the effect of the matrix on the execution of the analytical method. The level of the spike should be at the regulatory action level if this is thought to be several multiples of the amount of analyte present in the sample. The level of spiking should be significant with respect to the amount of analyte present in the sample. An alternative may be to incorporate a portion of a previously analyzed sample within the analytical

batch (a sample of a similar matrix) in order to reliably spike the sample. When the concentration of the analyte in the sample is such that the precedure is an assay rather than a residual determination (greater than 1%), no spike of the analyte is necessary.

Check Sample: Sample composed of standards in a matrix which causes minimum or no interferences.

Duplicate Sample: A duplicate sample is a portion of the sample of sufficient volume (or weight) to permit analysis in a manner identical to that of the original sample aliquot.

Duplicate Spike: An approach to combining the spiked and duplicate samples is to split a field sample in a ratio of 2:1. Spike the larger volume of sample and resplit that 1:1. This yields an unspiked field sample and a spiked duplicate sample.

Check Standard: Standard for checking calibration.

6.4 Calibration

6.4.1 Organic Analysis

Identification and quantification of all analytes must be accomplished with an authentic standard of the analyte. When authentic standards compounds are not

available, identification may be inferred (mass spectrometrically) using library or literature reference spectra. Quantification may be accomplished (semi-quantitatively) relative to a structurally similar compound. It is expected that every effort will be made to obtain standards.

Calibration curves must be set with a minimum of three concentrations spanning the linear range of the instrument using internal standards whenever possible.

For gas chromatographic identification, the relative retention time of the unknown is compared to that of an authentic standard. A minimum of one sample of each batch should be re-run on a column of different polarity to obtain a different relative retention time for compound confirmation by gas chromatography. For mass spectrometric identification, the relative retention time and mass spectrum of the analyte compared to an authentic standard obviate the need for a confirming column. The criteria for the matching of a mass spectrum are elaborated in Methods 8240 and 8270.

For the mass spectrometer, the spectrum of the analyte should conform to a literature representation of the spectrum or a spectrum of the authentic standard obtained within a working shift's time subsequent to satisfactorily tuning the mass spectrometer.

6.4.2 Metals Determination

ICP calibration requires determination of potential interferents in the samples. In order to accurately correct reponses, EPA analytical programs in hazardous wastes have successfully used the check sample composition in Table 5.

If sample conditions require a check standard of different relative composition, such check standards should be prepared and used.

6.5 Surrogate Compounds

Surrogate compounds serve two functions:

- They serve as analytical markers, i.e., the results of surrogate recoveries can be used to establish characteristic values for recovery to aid in an overall evaluation of precision and accuracy in the use of the analytical method.
- When sufficient data have been accumulated, a correlation may be established between the recovery of surrogates and the recovery of analytes.

Surrogates should be spiked into samples at levels sufficiently above the detection limit to obtain realistic precision estimates and recovery estimates of these compounds. Surrogates should not be spiked at the estimated detection limit to obtain values of precision and accuracy of recovery of these compounds. When possible, the regulatory action

TABLE 5

INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS
USED FOR ICP INTERFERENCE CHECK SAMPLE

Analytes	(mg/L)	Interferents	(mg/L)
Ag	0.5	Al	500
As	1.0	Ca	500
Ba	0.5	Fe	500
Be	0.5	Mg	500
Cd	1.0		
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
Sb	1.0		
Se	1.0		
Tl	1.0		
V	0.5		
Zn	1.0		

level is a useful concentration at which to spike samples. If there is no known action level, the spiking should be at five times an estimated detection level if such a concentration is analytically useful. For example, an estimated detection limit may be 50 ppb. A spiking concentration of 250 ppb will probably yield useful information concerning analytical performance. An estimated detection limit of 2000 ppm yielding a spiking level of 10,000 ppm indicates the method requires further modification to obtain analytical results at the residue level.

If the spiking level must exceed 100 ppm (0.01%) because analytes are above 0.01%, then surrogates are not required. Evaluation of analytical quality will rely on the quality control embodied in the check, spiked and duplicate samples.

6.6 Detection Limits

Detection limit of an analyte as a function of the analytical method should be calculated. This is the instrumental detection limit modified by the calculation necessitated by sample volume/weights and dilution or extraction/concentrations. It is recognized that interferents and contaminants have a marked affect on the detection limit. This affect should be estimated and a realistic detection limit calculated. This detection limit should be documented as a function of detector response for

spiked authentic analytes to field samples which are representative of waste stream or environmental stratum conditions.

6.8 Clean-Ups

6.8.1 All batches of florisil, alumina or silica gel prepared for clean-up should be checked for analyte recovery by running the elution with standards as a column check.

6.8.2 The elution pattern should be optimized for maximum recovery of analytes and maximum rejection of contaminants.

6.8.3 The elution pattern should be confirmed with a column check of standard compounds before each analytical batch is run through a set of columns. These compounds should be representative of each elution fraction.

6.8.4 A 90% or better recovery of the check standard compound is acceptable with a column check.

7.0 Deliverables

7.1 Analytical Results

. Analyte concentration

. Sample weight

. Water (%)

. Final volume of extract or diluted sample

7.2 Calibration

. Calibration curve or coefficients of the linear equation which describes the calibration curve.

. Correlation coefficient of the linear calibration.

. Concentration/Response (or relative response) of the calibration check standards along with dates they were analytically determined.

7.3 Column Check

Results of column chromatography check should be reported along with the chromatogram for the column check.

7.4 Extraction/Digestion

. The date of the extraction for each sample should be reported.

7.5 Surrogates

. Amount of surrogate spiked and percent recovery of each surrogate should be reported for each sample.

7.6 Duplicate Spikes

. Amount spiked and percent recovery should be reported for each compound in the spiked samples for the batch.

7.7 Check Sample

. Amount spiked and percent recovery of each compound spiked should be reported.

7.8 Blank

. Identity and amount of each constituent should be reported.

7.9 Chromatograms (for organic analysis)

. All chromatograms for reported results and a representation calibration should be provided.

. All chromatograms should be properly labeled.

Proper labeling includes:

- Sample identification
- Method identification
- Identification of retention time of
. analyte on the chromatograms

7.10 Quantitative Chromatogram Report

. Retention time of analyte
. Amount injected
. Area or appropriate calculation of detection reponse
. Amount of analyte found
. Date and time of injection

7.11 Mass Spectrum

- Spectra of standards generated from authentic standards (once for each report)

- Spectra of analytes from actual analyses
- Spectrometer identifier

7.12 Metal Interference Check Sample Results

7.13 Detection Limit

Analyte detection limit with methods of estimation